

Electroviscous effects of simple electrolytes under shear

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Abstract. On the basis of a hydrodynamical model analogous to that in critical fluids, we investigate the influences of shear flow upon the electrostatic contribution to the viscosity of binary electrolyte solutions in the Debye-Hückel approximation. Within the linear-response theory, we reproduce the classical limiting law that the excess viscosity is proportional to the square root of the concentration of the electrolyte. We also extend this result for finite shear. An analytic expression of the anisotropic structure factor of the charge density under shear is obtained, and its deformation at large shear rates is discussed. A non-Newtonian effect caused by deformations of the ionic atmosphere is also elucidated for $\tau_D \dot{\gamma} > 1$. This finding concludes that the maximum shear stress that the ionic atmosphere can support is proportional to λ_D^{-3} , where $\dot{\gamma}$, λ_D and $\tau_D = \lambda_D^2/D$ are, respectively, the shear rate, the Debye screening length and the Debye relaxation time with D being the relative diffusivity at the infinite dilution limit of the electrolyte.

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1. Introduction

It is deeply recognized that the long-ranged Coulomb interaction between ions gives rise to the viscosity enhancement of electrolyte solutions [1, 2, 3, 4]. When a velocity gradient in the solution will deform an ionic atmosphere (a cloud of counterions around an ion), which would otherwise possess a spherical symmetry, electrostatic forces as well as thermal motion tend to restore the atmosphere to its original form. Because of a finite relaxation time of the ionic atmosphere, these two effects can be balanced in a stationary state. This effect is closely related to the relaxation effect in conductance, and also it is sometimes called the “electroviscous” effect by analogy with the electroviscous effects found in charged colloidal suspensions [3]. In the case of very low concentration, such an ionic effect is proportional to the square root of the concentration, as was found many years ago by Falkenhagen [5] and Onsager and Fuoss [6, 7] theoretically, and by Jones and Dole experimentally [8].

The concentration dependence of the transport properties (such as the conductivity and the viscosity) of electrolyte and polyelectrolyte solutions still offer significant challenges. Today, there exists a large number of theoretical and numerical studies that take into account realistic structural effects of ions and polyions. Among them, one of the most celebrated is the mode coupling theory combined with accurate pair correlation functions of liquids [9], which has recently made considerable progress in this area [10, 11, 12, 13, 14]. With regard to the study of viscosity, however, most of the literature has concentrated on the intrinsic viscosity.

To the best of our knowledge, nonlinear responses of electrolyte solutions in velocity field remains largely unexplored so far, even in the infinite dilution limit. The aim of this paper is therefore to study how a strong shear flow modifies the “electroviscous effect” mentioned above. Because analytic calculations of general cases are impossible, we will consider in this paper a binary electrolyte solution in very low concentration, for which analytic expressions of various statistical quantities are available. Our formulation is in principle applicable over an unrestricted range of field intensities as far as the local-equilibrium condition is not severely violated. Although the present work is limited to the specific simple system and thus might be less noticeable in the practical point of view, we expect that this work may prompt further studies towards better understandings of rheological properties in more important systems such as concentrated electrolyte solutions, polyelectrolyte solutions [15] and charged colloidal suspensions [16, 17] under shear.

This paper is organized as follows. In Sec. II, we set up Langevin equations for fluctuating concentration of ions combined with the free energy functional which accounts for electrostatic interactions within Debye-Hückel approximation. Our model is directly employed from that in critical fluid binary mixtures [18, 19]. The linear response is first studied in Sec. III. We show a smart derivation of Falkenhagen-Onsager-Fuoss limiting law [5, 6, 7] for binary electrolyte solutions. In Sec IV, an anisotropic structure factor of charge density and the excess viscosity are explicitly obtained as a

function of the shear rate. The limitation and the experimental relevancy of our results are discussed in Sec V, followed by our brief summary in the last section.

2. Model Equations

2.1. Free Energy

Consider an electrolyte solution consisting of only two kinds of ions dissolved in a continuum solvent of dielectric constant ϵ , each of which carries charges Ze and $-e$ (e is the elementary charge). The average number density of the two ion species are written as $\langle n_+ \rangle = \bar{n}$ and $\langle n_- \rangle = Z\bar{n}$, respectively. Then the total ion number density is given by $n_{tot} = (Z + 1)\bar{n}$. The free energy of this system is composed of the entropic and electrostatic contributions:

$$F = \int \left[f + \frac{1}{2} \int \rho_c \phi \right] d\mathbf{r}. \quad (1)$$

The first term of the right-hand side of Eq. (1) is the entropic contribution of ideal mixing given by [18]

$$f = k_B T \sum_{\alpha} \left[n_{\alpha} \ln(n_{\alpha} a^3) - n_{\alpha} \right], \quad (2)$$

where $n_{\alpha}(\mathbf{r})$ is the number density of the ion species α , T the temperature, k_B the Boltzmann constant, and the two kinds of ions have a common radius a . The charge density is thus given by $\rho_c(\mathbf{r}) = Ze n_+(\mathbf{r}) - e n_-(\mathbf{r}) = e Z \bar{n} \psi(\mathbf{r})$, where we have introduced the variable ψ as the order parameter of the charge density fluctuation. The second term in the free energy F is the electrostatic contribution. The electrostatic potential satisfies the Poisson equation

$$\nabla^2 \phi(\mathbf{r}, t) = -\frac{4\pi}{\epsilon} \rho_c(\mathbf{r}, t). \quad (3)$$

Note that the time dependence of the electrostatic potential entirely comes from slow variations of the charge density $\rho_c(\mathbf{r}, t)$ due to relative diffusion between oppositely charged molecules. Introducing the Coulomb operator $v(\mathbf{r})$ which satisfies $\nabla^2 v(\mathbf{r}) = -4\pi\delta(\mathbf{r})$, we can write the formal solution of Eq. (3) as

$$\phi(\mathbf{r}, t) = \frac{1}{\epsilon} \int d\mathbf{r}' v(\mathbf{r} - \mathbf{r}') \rho_c(\mathbf{r}', t). \quad (4)$$

Assuming the total number density of ions is nearly constant everywhere: $n_+(\mathbf{r}) + n_-(\mathbf{r}) \cong n_{tot}$, Eq. (2) can be expanded in powers of ψ . Up to the quadratic order, we find $f \cong \psi^2/2\chi$, where $\chi = (Z + 1)/(Z\bar{n})$ is the osmotic compressibility. Substituting these equations into Eq. (1), we obtain the free energy relevant to our purpose in the form

$$\beta F = \int d\mathbf{r} \frac{1}{2\chi} \psi^2 + \frac{Z^2 \ell_B \bar{n}^2}{2} \int d\mathbf{r} \int d\mathbf{r}' \psi(\mathbf{r}) v(\mathbf{r} - \mathbf{r}') \psi(\mathbf{r}'), \quad (5)$$

where $\beta = 1/k_B T$ and the Bjerrum length $\ell_B = e^2/\epsilon k_B T$ is defined as the length at which the Coulomb energy between two elementary charges becomes comparable to thermal energy $k_B T$.

2.2. Dynamic Equations

To describe the dynamics of the charge fluctuation $\delta\rho_c = Ze\bar{n}\delta\psi$ and to calculate the shear viscosity under steady shear flow, we start with the following generalized Langevin equations (see also Appendix)

$$\frac{\partial}{\partial t}\psi = -\mathbf{v} \cdot \nabla\psi - L\nabla^2 \frac{\delta}{\delta\psi}(\beta F) + \theta, \quad (6)$$

$$\bar{\rho} \frac{\partial}{\partial t}\mathbf{v} = -\nabla p - k_B T \psi \nabla \frac{\delta}{\delta\psi}(\beta F) + \eta_0 \nabla^2 \mathbf{v} + \mathbf{f}, \quad (7)$$

where the generalized diffusion equation for ψ is now coupled with the velocity field of the fluid \mathbf{v} through the reversible term $-\mathbf{v} \cdot \nabla\psi$. The pressure p in Eq. (7) is determined so as to satisfy the incompressibility condition $\nabla \cdot \mathbf{v} = 0$. The Gauss-Markov thermal noise source $\theta(\mathbf{r}, t)$ and $\mathbf{f}(\mathbf{r}, t)$ are related to the kinetic coefficients L and the zero-shear viscosity η_0 via the usual fluctuation-dissipation relations given by

$$\langle \theta(\mathbf{r}, t) \theta(\mathbf{r}', t') \rangle = -2L \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \quad (8)$$

$$\langle f_i(\mathbf{r}, t) f_j(\mathbf{r}', t') \rangle = -2\eta_0 k_B T \nabla^2 \delta(\mathbf{r} - \mathbf{r}') \delta(t - t') \delta_{ij}. \quad (9)$$

The second term on the right-hand side of Eq. (7) represents the force exerted to the fluid by the deviation of ψ from its equilibrium value $\langle \psi \rangle = 0$. This term should be incorporated in Eq. (7) as the counterpart of the reversible mode-coupling term $-\mathbf{v} \cdot \nabla\psi$ in Eq. (6) in order to ensure that the equilibrium distribution of ψ and \mathbf{v} is given by the Boltzmann distribution $\exp(-F/k_B T - \frac{\bar{\rho}}{2} \int d\mathbf{r} \mathbf{v}^2 / k_B T)$. Neglecting the random force, we can rewrite Eq. (7) in the form which suggests the momentum conservation

$$\frac{\partial}{\partial t}(\bar{\rho}\mathbf{v}) + \nabla \cdot \mathbf{\Pi} = 0, \quad (10)$$

where the stress tensor is written as

$$\Pi_{ij} = \left(p + \frac{k_B T}{2\chi} \psi^2 \right) \delta_{ij} - \frac{\epsilon}{4\pi} \partial_i \phi \partial_j \phi - \eta_0 (\partial_i v_j + \partial_j v_i). \quad (11)$$

The second term $-(\epsilon/4\pi) \partial_i \phi \partial_j \phi$ comes from the long-ranged interionic Coulomb interactions and is nothing but the Maxwell stress tensor [20]. When the average velocity field $\langle \mathbf{v} \rangle = \dot{\gamma} y \mathbf{e}_x$ is imposed in this system, the corresponding shear stress is thus given by

$$\sigma_{xy} = -\langle \Pi_{xy} \rangle = \eta_0 \dot{\gamma} + \frac{\epsilon}{4\pi} \left\langle \frac{\partial \phi}{\partial x} \frac{\partial \phi}{\partial y} \right\rangle. \quad (12)$$

Note that the second term in this equation gives rise to the electroviscous effect in a sheared electrolyte solution.

3. Linear Response Theory: The Limiting Law

In this section, we shall discuss the electrostatic contribution to the viscosity within the linear response theory. Because we are interested in the macroscopically homogeneous

state ($\langle\psi\rangle = 0$) far from its critical point, we can linearize Eq. (6) to obtain

$$\frac{\partial}{\partial t}\psi = -\mathbf{u} \cdot \nabla\psi - D(\nabla^2 + \kappa_D^2)\psi + \theta, \quad (13)$$

where $\mathbf{u} = \langle\mathbf{v}\rangle$, and where we have defined the relative diffusivity $D = L/\chi$ and the inverse Debye screening length $\kappa_D = 1/\lambda_D$ as

$$\kappa_D^2 = 4\pi\ell_B Z^2 \bar{n}^2 \chi = \frac{4\pi Z e^2 n_{tot}}{\epsilon k_B T}. \quad (14)$$

In the absence of the macroscopic flow $\mathbf{u} = 0$, Eq. (13) can be easily solved to yield the dynamic structure factor

$$S(k, t) = \frac{\langle\psi_{\mathbf{k}}(t)\psi_{\mathbf{k}'}(0)\rangle}{(2\pi)^3\delta(\mathbf{k} + \mathbf{k}')} = \frac{\chi k^2}{k^2 + \kappa_D^2} \exp[-D(k^2 + \kappa_D^2)t]. \quad (15)$$

Here, the Fourier transform of ψ is defined by

$$\psi(\mathbf{r}, t) = \int \frac{d^3\mathbf{k}}{(2\pi)^3} \exp(i\mathbf{k} \cdot \mathbf{r}) \psi_{\mathbf{k}}(t). \quad (16)$$

The intrinsic viscosity including the electrostatic contribution η can be calculated by making use of the Green-Kubo formula [18]:

$$\eta = \eta_0 + \frac{1}{k_B T} \int_0^\infty dt \int d\mathbf{r} \langle \hat{\Pi}_{xy}(\mathbf{r}, t) \hat{\Pi}_{xy}(\mathbf{0}, 0) \rangle, \quad (17)$$

where the electrostatic shear stress is given by $\hat{\Pi}_{xy} = \epsilon/4\pi(\partial\phi/\partial x)(\partial\phi/\partial y)$. Within the Gaussian approximation, the four-body correlation between ϕ appearing in the right-hand side of Eq. (17) can be decoupled into the product of the pair correlation of ϕ . Noting that the Fourier transform of Eq. (3) gives $\phi_{\mathbf{k}}(t) = 4\pi Z e \bar{n} (\epsilon k^2)^{-1} \psi_{\mathbf{k}}(t)$ and using (15), we can readily integrate over time in Eq. (17) to find

$$\eta = \eta_0 + \frac{k_B T}{D} \kappa_D^4 \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{k_x^2 k_y^2}{k^4 (k^2 + \kappa_D^2)^3} \quad (18)$$

Performing the integration over \mathbf{k} , we finally obtain $\eta = \eta_0 + c_1 k_B T \kappa_D / D$, where the numerical constant c_1 is given by

$$c_1 = \frac{1}{(2\pi)^3} \int_0^{2\pi} \sin^2 \varphi \cos^2 \varphi d\varphi \int_0^\pi \sin^5 \theta d\theta \int_0^\infty \frac{x^2 dx}{(1+x^2)^3} = \frac{1}{480\pi}. \quad (19)$$

The relative diffusivity D in Eq. (13) has been originally introduced in the context of “collective” meaning. In the limit of the infinite dilution, however, D coincides with the self diffusivity of a tagged ion, D_s , which is related to the mobility of the tagged ion μ via the Einstein relation $D_s = \mu k_B T$. Therefore, by defining the friction constant of a tagged ion as $\gamma = \mu^{-1}$, one can recover the limiting law originally derived by Falkenhagen for binary electrolytes [5] (and later rederived by Fuoss and Onsager for more general multicomponent cases [6, 7]), which is written as

$$\Delta\eta_0 = \eta - \eta_0 = \frac{\kappa_D \gamma}{480\pi}. \quad (20)$$

This simple scaling concludes the well-known fact that the viscosity enhancement is proportional to the square root of the electrolyte concentration. A similar derivation of Eq. (20) can be also found in the recent literature [12, 13].

4. Nonlinear Effects

Let us proceed to investigate how the electroviscous effect is modified in the presence of steady shear flow. In the case of simple shear $\mathbf{u} = \dot{\gamma}y\mathbf{e}_x$, \mathbf{e}_x being the unit vector along the x axis, the diffusion equation (13) in the Fourier space becomes

$$\left[\frac{\partial}{\partial t} - \dot{\gamma}k_x \frac{\partial}{\partial k_y} \right] \psi_{\mathbf{k}}(t) = -D(k^2 + \kappa_D^2)\psi_{\mathbf{k}}(t) + \theta_{\mathbf{k}}(t). \quad (21)$$

Applying the standard manipulation described somewhere [21], we find the solution of Eq. (21) in the form

$$\psi_{\mathbf{k}}(t) = \int_0^\infty \theta_{\mathbf{k}(s)}(t-s)G(\mathbf{k}, s)ds, \quad (22)$$

where $\mathbf{k}(t)$ is the time-dependent wave vector defined by $\mathbf{k}(t) = \mathbf{k} + \dot{\gamma}k_x t\mathbf{e}_y$, and the Green's function is given by

$$G(\mathbf{k}, t) = \exp \left[-D \int_0^t ds (\mathbf{k}^2(s) + \kappa_D^2) \right]. \quad (23)$$

Using the correlation property Eq. (8), we find that the steady-state structure factor is given by

$$S(\mathbf{k}) = 2L \int_0^\infty \mathbf{k}^2(s)G^2(\mathbf{k}, s)ds. \quad (24)$$

If we introduce the dimensionless variables $\mathbf{q} = (D/\dot{\gamma})^{1/2}\mathbf{k}$ and $l = \dot{\gamma}s$, Eq. (24) can be rewritten as $S(\mathbf{k}) = \chi \tilde{S}(\mathbf{q})$, where $\tilde{S}(\mathbf{q})$ is explicitly given by

$$\tilde{S}(\mathbf{q}) = 1 - \frac{2}{\tau_D \dot{\gamma}} \int_0^\infty dl \exp \left[-2 \left\{ \left(q^2 + \frac{1}{\tau_D \dot{\gamma}} \right) l + q_x q_y l^2 + \frac{1}{3} q_x^2 l^3 \right\} \right]. \quad (25)$$

The Debye relaxation time τ_D defined by $\tau_D = \lambda_D^2/D = \epsilon k_B T / (4\pi Z e^2 n_{tot} D)$ represents the time scale at which the deformed ionic atmosphere around an ion recovers its equilibrium spherical form. The dimensionless quantity $\tau_D \dot{\gamma}$ is therefore regarded as the control parameter which measures the relative strength of the shear flow (external perturbation) to the stability inherent to this system. Numerically evaluated $\tilde{S}(\mathbf{q})$ for two different values of $\tau_D \dot{\gamma}$ is displayed in Fig. 1. For $\tau_D \dot{\gamma} > 1$, the structure factor is considerably deformed by the shear, and rapidly reaches the unity as q_x increases, reflecting the enhanced homogeneization along the flow direction by the shear.

These dramatic changes of $S(\mathbf{k})$ due to shear should also affect the ionic contribution to the viscosity. According to Eq. (12), the excess shear stress is given by

$$\sigma_{xy}(\dot{\gamma}) = \frac{\epsilon}{4\pi} \left(\frac{4\pi Z e \bar{n}}{\epsilon} \right)^2 \int \frac{d^3 \mathbf{k}}{(2\pi)^3} \frac{k_x k_y}{k^4} S(\mathbf{k}). \quad (26)$$

As is obvious from the spherical symmetry, $\sigma_{xy}(\dot{\gamma} = 0)$ is zero. However, to avoid apparent divergence of the integrand in Eq. (26) in the limit of $s = 0$, we hereafter consider the quantity $\Delta\sigma_{xy}(\dot{\gamma}) = \sigma_{xy}(\dot{\gamma}) - \sigma_{xy}(0)$. Introducing the polar coordinate and integrating over $k = |\mathbf{k}|$, we have

$$\Delta\sigma_{xy}(\dot{\gamma}) = \frac{1}{8} \frac{k_B T \kappa_D^2}{(2\pi)^{5/2} D^{1/2}} \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta a(\theta, \varphi)$$

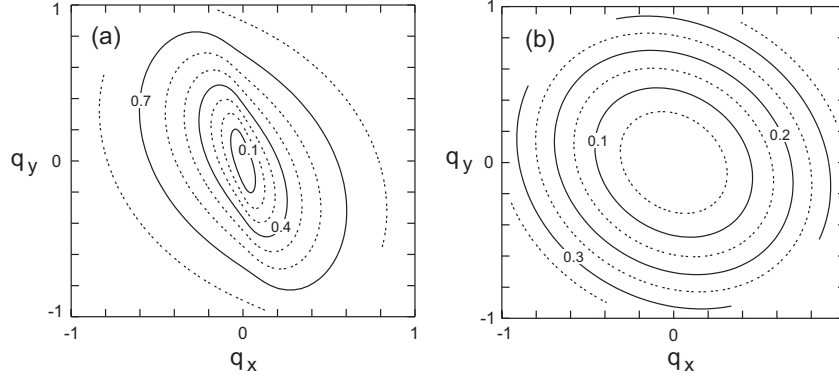


Figure 1. Contour plots in the shear plane of the steady-state structure factor $\tilde{S}(\mathbf{q})$ for shear rates (a) $\tau_D \dot{\gamma} = 5.0$ and (b) $\tau_D \dot{\gamma} = 0.5$.

$$\times \int_0^\infty ds e^{-D\kappa_D^2 s} \left[\frac{1 + 2a(\theta, \varphi)\dot{\gamma}s + b(\theta, \varphi)\dot{\gamma}^2 s^2}{(s + a(\theta, \varphi)\dot{\gamma}s^2 + \frac{1}{3}b(\theta, \varphi)\dot{\gamma}^2 s^3)^{3/2}} - \frac{1}{s^{3/2}} \right]. \quad (27)$$

where $a(\theta, \varphi) = \sin^2 \theta \cos \varphi \sin \varphi$ and $b(\theta, \varphi) = \sin^2 \theta \cos^2 \varphi$ have been introduced. Integrating further over s by parts, we finally arrive at the following result after some algebra,

$$\Delta\eta(\dot{\gamma}) = \frac{1}{\dot{\gamma}} \Delta\sigma_{xy}(\dot{\gamma}) = \Delta\eta_0 H(\tau_D \dot{\gamma}), \quad (28)$$

where $\Delta\eta_0 = (480\pi D)^{-1} k_B T \kappa_D$ is the excess viscosity derived in the last section. The scaling function $H(x)$ is written as

$$H(x) = \frac{240}{(2\pi)^{3/2}} \frac{1}{x} \int_0^\infty e^{-2u^2} J(xu^2) du, \quad (29)$$

where

$$J(y) = \int_0^{2\pi} d\varphi \int_0^\pi d\theta \sin \theta a(\theta, \varphi) \left[1 - \frac{1}{(1 + a(\theta, \varphi)y + \frac{1}{3}b(\theta, \varphi)y^2)^{1/2}} \right] \quad (30)$$

By expanding $J(xu^2)$ in powers of x , one can easily check $H(x) = 1 - b_1 x^2 + \dots$ for $x \ll 1$, where $b_1 = 15/128$. The present theory therefore correctly reduces to the Falkenhagen-Onsager-Fuoss expression of the excess viscosity in the zero-shear limit. For small $\tau_D \dot{\gamma}$, the excess viscosity is the analytic function of $\dot{\gamma}$ and exhibits a weak shear-thinning given by

$$\Delta\eta(\dot{\gamma}) = \Delta\eta_0 \left[1 - \frac{15}{128} (\tau_D \dot{\gamma})^2 + \dots \right]. \quad (31)$$

5. Discussion

The numerical evaluation of the scaling function $H(x)$ is shown in Fig. 2. As can be seen in Fig. 2 (a), the excess viscosity $\Delta\eta$ rapidly decreases much below the intrinsic

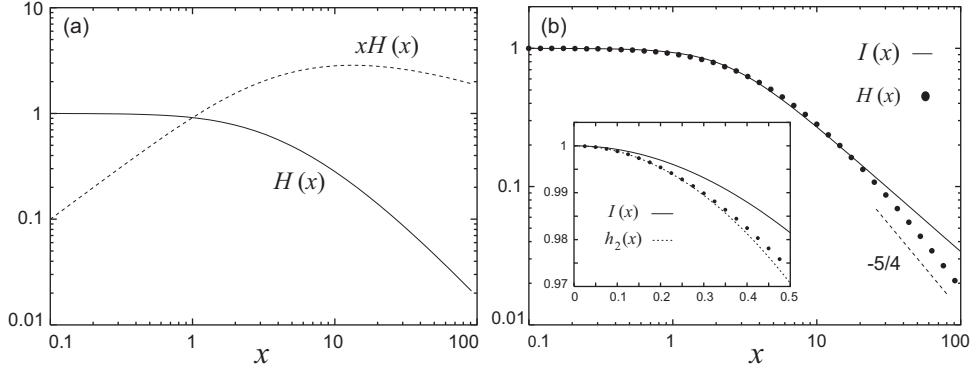


Figure 2. (a) Plots of numerically evaluated scaling functions $H(x)$ and $xH(x)$. (b) Comparison between (numerically evaluated) $H(x)$ and the fitting function $I(x)$ [Eq. (32)].

value $\Delta\eta_0$ as the shear rate exceeds $\dot{\gamma}_c = \tau_D^{-1}$. The overall behavior of $H(x)$ up to $x \sim 20$ are fairly well fitted by the empirical function $I(x)$ of the form

$$I(x) = \frac{1}{[1 + \lambda x^2]^\alpha}, \quad (32)$$

where $\lambda \cong 0.17$ and $\alpha \cong 0.46$ in Fig. 2 (b). For small enough x , however, $h_2(x) = 1 - b_1 x^2$ (the Taylor expansion of $H(x)$ around $x = 0$ which we have obtained in the last section) actually fits better to the numerical data of $H(x)$ than $I(x)$, as shown in the inset of Fig. 2 (b). Roughly speaking, therefore, the excess viscosity behaves as $\Delta\eta \sim \dot{\gamma}^{-2\alpha}$ for $1 < \tau_D \dot{\gamma} < 20$, and even more strongly decreases as $\Delta\eta \sim \dot{\gamma}^{-5/4}$ for larger $\tau_D \dot{\gamma}$.

Correspondingly, the excess shear stress $\Delta\sigma_{xy}$ saturates into its maximum value $\Delta\sigma_m \sim \Delta\eta_0 \dot{\gamma}_c \sim c_1 k_B T / \lambda_D^3$ at $\tau_D \dot{\gamma} \sim 10$, and then slowly decreases for larger $\dot{\gamma}$. If one considers the “effective surface tension” a_s of an ionic atmosphere of size λ_D on analogy with a droplet in an immiscible fluid, one would obtain $a_s \sim k_B T / \lambda_D^2$ from the energy balance condition. Assuming that the pressure difference between interior and exterior of the droplet can be balanced by the imposed shear stress, $a_s / \lambda_D \sim \Delta\sigma_m$, one immediately recovers the above expression of $\Delta\sigma_m$.

Let us examine the magnitude of the predicted shear-thinning effect. For the zero-shear viscosity at higher concentrations, the following empirical equation:

$$\Delta\eta_0(c) = A\sqrt{c} + Bc, \quad (33)$$

provides a better description of the experimental results. The constant A was evaluated from experimental data for various salts by plotting a suitable form of Eq. (33), and the good agreement with the theory has been obtained for aqueous solutions [4]. However, the absolute magnitude of this contribution to the viscosity ($A\sqrt{c}$ term) is found to be rather small (as can be seen in the large number (480π) in the denominator of Eq. (20)). Usually, more significant contribution comes from the ion-solvent interaction, which is represented by the Bc term in Eq. (33), but there is no satisfactory theoretical explanation of the coefficient B in Eq. (33) so far. The present study

suggests that, at strong shear as $\tau_D \dot{\gamma} \sim 10$, the coefficient A decreases to 20% of its original value. Therefore, while a direct experimental observation of the shear-thinning would be hard because of the vanishingly small value of A , the modified fitting function $\Delta\eta_0/\eta_0 \cong 1 + Bc$, which tells the linear dependence of the viscosity upon the concentration, might be best fitted to experimental data under strong shear conditions (provided that the linear concentration dependence arising from the ion-solvent interaction is not significantly changed by the shear). Although indirect, this may serve a possible experimental verification of the shear-thinning effect in future experiments.

At very large shear $\tau_D \dot{\gamma} \gg 1$, the ionic atmosphere is no longer ellipsoidal because it is dramatically stretched by the shear, and dissipates thermally. The considerably deformed atmosphere may not support the shear stress any more, and $\Delta\sigma_{xy}$ itself is thus decreased. If we use typical values of the diffusion constant $D \sim 10^{-5} \text{ cm}^2\text{sec}^{-1}$ and the Debye screening length $\lambda_D \sim 3 \times 10^{-7} \text{ cm}$ for 0.01 M solutions of strong 1:1 electrolytes (like NaCl in water), we find $\dot{\gamma}_c \sim 10^8 \text{ sec}^{-1}$, which is unrealistically large. This simple estimation suggests that, unfortunately, even the strong shear condition $\tau_D \dot{\gamma} \sim 1$ might be difficult to be realized in ordinary experimental setup. In other words, the ionic contribution to the viscosity may not be significantly influenced by the shear in most realistic conditions.

Experimentally, however, a near-critical ionic fluid, in which the charge density fluctuation decays slowly, can be prepared by carefully choosing materials and by controlling the temperature [22, 23, 24, 25]. In that case, the correlation decays as $\exp(-D_R k^2 t)$, where the (renormalized) diffusion constant may be given by Kawasaki-Stokes's law $D_R \sim k_B T / 6\pi\eta\xi$ with ξ being the correlation length of the critical fluctuations [18, 19]. Although a rather crude argument, we naively expect $\dot{\gamma}_c \sim 3 \times 10^4 \text{ sec}^{-1}$, which is still very large but is much lower than that for an ordinary electrolyte solution, as well as a relatively large magnitude of the electroviscous effect on the order of $\Delta\eta_0/\eta_0 \cong \frac{1}{80} \kappa_D \xi \sim 0.1$, if we assume $\eta_0 \sim 40 \text{ cP}$, $\xi \sim 10 \text{ nm}$, $\lambda_D \sim 1 \text{ nm}$ for $T = 343 \text{ K}$, which are the typical value set for (Bu₄NPic)-tridecane-1-ol. (This model system shows liquid-liquid phase separation with an upper consolute point near 342K, expected to be driven by Coulombic interaction [23].) Needless to say, in order for a more accurate treatment of an ionic fluid near a demixing or a gas-liquid transition, we have to take into consideration the density gradient term $(\nabla\psi)^2$ in F which accounts for the spatial heterogeneity of critical fluctuations (and becomes more and more important as the system approaches the critical point). Our rough estimation therefore might be appropriate only in pre-stages of a critical regime. In this connection, the free energy Eq.(5) including the gradient term is mathematically equivalent to that of diblock copolymer systems derived by Ohta and Kawasaki [26], in which the long-range interaction arising from the connectivity of different chemical sequences in a polymer chain plays a crucial role. Its close similarity to charged fluids has also been pointed out in the literature [26]. Near-critical properties of that system under shear in one phase region was also studied by Onuki based on the same dynamic equations employed

here [27]. On the other hand, in molecular dynamics simulations, accessible shear rates are much larger than those in real experiments, and the strong shear condition will be easily realized [28, 29]. Then the pronounced shear-thinning behavior predicted here would be more likely to be checked by computer simulations.

The increase and saturation of ionic conductivity of electrolyte solutions at very high applied voltage is known as Wien effect [1, 30, 31]. This increase has been shown in general to arise from two different effects, namely, a destruction of the ionic atmosphere and a modification of the dissociation kinetics [30]. In strong electrolytes the former effect can dominate over the latter. It is instructive to remark that the similar mechanism works in the system we studied here, that is, the destruction of the ionic atmosphere by strong shear renders the increase and saturation of the reciprocal of the viscosity, *i.e.*, the fluidity.

6. Conclusion

We now summarize our results. Effects of shear flow on the viscosity of electrolyte solutions are studied theoretically within the framework of fluctuating hydrodynamics. Our calculations confirm the Falkenhagen-Onsager-Fuoss limiting law that the ionic effects to the viscosity is proportional to the square root of the concentration of the electrolytes in the dilute and the zero-shear limit. We extend this classical result for finite shear by deriving the analytic expression of the excess nonlinear shear viscosity. The electrostatic contribution to the viscosity is drastically reduced under the strong shear condition $\tau_D \dot{\gamma} > 1$, which however might be difficult to access experimentally. Because the use of Debye-Hückel theory here limits the applicability of our treatment to low concentration solutions, the viscoelasticity of concentrated electrolyte solutions under shear is an important remaining problem. Studies in this direction using Brownian Dynamics simulation is currently in progress. We hope that this work will prompt further studies on the nonlinear transport theory of electrolyte solutions in large velocity fields, which might constitute the counterpart of the conductivity studies in large driving fields.

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Appendix A. Derivation of the dynamic equations

In this Appendix, we describe the derivation of the dynamical equations (6) and (7) based on a two-fluid model for electrolyte solutions. We will specifically consider strongly dissociative salt solutions such as NaCl and KCl in water. Such a solution

should be modelled as a three-fluid model, namely, as a mixture of dissolved positive ions, negative ions and the solvent. For simplicity, however, we will start from the two-fluid model for positive and negative ions, while regarding the solvent as the structureless background with a static dielectric constant ϵ . A number of approximations and simplifications involved at this stage are to be critically checked in future studies. (The present formulation is convenient to directly obtain a mutual diffusion equation for electrolyte solutions coupled with the Navier-Stokes equation. However, in order to obtain a diffusion equation for each ion species with vanishing electrostatic interactions, we also have to take into account hydrodynamic drag forces between ions and solvent molecules, which are not explicitly included in the present formulation. A more precise and systematic treatment for diffusion equations can be found, for example, in Ref. [32].)

The number conservation law for the ionic species $\alpha = \pm$ is written as

$$\frac{\partial n_\alpha}{\partial t} + \nabla \cdot (n_\alpha \mathbf{v}_\alpha) = 0, \quad (\text{A.1})$$

while the total density $n_{tot} = n_+ + n_-$ obeys the usual continuity equation

$$\frac{\partial n_{tot}}{\partial t} + \nabla \cdot (n_{tot} \mathbf{v}) = 0, \quad (\text{A.2})$$

where the average velocity \mathbf{v} is defined by

$$n_{tot} \mathbf{v} = n_+ \mathbf{v}_+ + n_- \mathbf{v}_-. \quad (\text{A.3})$$

Assuming that a fluid under consideration shows a vanishingly small compressibility in long-time scales, we set $\nabla \cdot \mathbf{v} = 0$ (the incompressibility condition), which implies from Eq. (A.2) that the total number density is constant, $n_{tot} \cong \bar{n}_{tot} = (Z + 1)\bar{n}$, for a sufficiently slow fluid motion where $\partial_t n_{tot}$ can be neglected. Introducing a relative velocity between the positive and negative ions by $\mathbf{u} = \mathbf{v}_+ - \mathbf{v}_-$, we can write the velocities of the two ion species as

$$\mathbf{v}_+ = \mathbf{v} + \frac{n_-}{n_{tot}} \mathbf{u}, \quad \text{and} \quad \mathbf{v}_- = \mathbf{v} - \frac{n_+}{n_{tot}} \mathbf{u}. \quad (\text{A.4})$$

Since we have defined a scaled charge density fluctuation as $Ze\bar{n}\psi(\mathbf{r}) = Zen_+(\mathbf{r}) - en_-(\mathbf{r})$, we find from Eqs. (A.1) and (A.4) the equations for ψ :

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\psi \mathbf{v}) = -\nabla \cdot \left[\frac{1}{Z} \frac{n_+ n_-}{\bar{n}^2} \mathbf{u} \right]. \quad (\text{A.5})$$

On the other hand, the equations of motions for the two ions species may be given by

$$mn_+ \frac{\partial \mathbf{v}_+}{\partial t} = -n_+ \nabla \mu_+ + \eta_+ \nabla^2 \mathbf{v}_+ - \zeta \mathbf{u}, \quad (\text{A.6})$$

$$mn_- \frac{\partial \mathbf{v}_-}{\partial t} = -n_- \nabla \mu_- + \eta_- \nabla^2 \mathbf{v}_- + \zeta \mathbf{u}, \quad (\text{A.7})$$

where m is the equal mass for two ion species, η_α is the viscosity, μ_α is the appropriately defined chemical potential, and ζ is the friction constant between the two ion species. Note that ζ may be given in terms of the friction constant of the each ion species ζ_α by $\zeta^{-1} = \zeta_+^{-1} + \zeta_-^{-1}$. Subtracting Eq. (A.7) from Eq. (A.6), we obtain the equation for the relative velocity \mathbf{u} as

$$\frac{\partial \mathbf{u}}{\partial t} = -\frac{1}{m} \nabla (\mu_+ - \mu_-) - \frac{\zeta}{m} \left(\frac{1}{n_+} + \frac{1}{n_-} \right) \mathbf{u}, \quad (\text{A.8})$$

where the viscosity terms have been neglected. Since we are concerned with very slow motion whose characteristic frequencies are much lower than $\zeta(1/n_+ + 1/n_-)$, we can set $\partial_t \mathbf{u} = 0$ in Eq. (A.8) to obtain

$$\mathbf{u} \cong - \left(\frac{1}{n_+} + \frac{1}{n_-} \right)^{-1} \frac{1}{\zeta} \nabla (\mu_+ - \mu_-). \quad (\text{A.9})$$

Here the chemical potential difference between two components are connected to the free energy as

$$\mu_+ - \mu_- = \frac{\delta F}{\delta n_+} - \frac{\delta F}{\delta n_-} = \text{const} + \chi \frac{\delta F}{\delta \psi}, \quad (\text{A.10})$$

where F is the free-energy functional in our model, and $\chi = (Z + 1)/(Z\bar{n})$. In differentiating F with respect to n_+ (n_-), we fix n_- (n_+) in Eq. (A.10). This relation can be directly checked by using the explicit form of F given in the main text. Substituting Eq. (A.9) into Eq. (A.5) with Eq. (A.10), we obtain

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\psi \mathbf{v}) = L \nabla^2 \frac{\delta}{\delta \psi} (\beta F), \quad (\text{A.11})$$

where $\beta = 1/k_B T$ and the kinetic coefficient

$$L = \frac{k_B T}{Z} \frac{\chi (\bar{n}_+ \bar{n}_-)^2}{\bar{n}^2 \bar{n}_{tot}} = \frac{k_B T}{\zeta}, \quad (\text{A.12})$$

is independent of ψ . On the other hand, by adding Eq. (A.6) and (A.7), the equation for the average velocity \mathbf{v} is found to become

$$m \bar{n}_{tot} \frac{\partial \mathbf{v}}{\partial t} = -(n_+ \nabla \mu_+ + n_- \nabla \mu_-) + (\eta_+ + \eta_-) \nabla^2 \mathbf{v}, \quad (\text{A.13})$$

where the use of Eq. (A.4) has been made, and only fluctuations up to the linear order have been retained. Again, by using the explicit form of the free energy functional, one can directly check the relation

$$n_+ \nabla \mu_+ + n_- \nabla \mu_- = \nabla p - \psi \nabla \frac{\delta F}{\delta \psi}, \quad (\text{A.14})$$

where p can be regarded as the hydrostatic pressure of the fluid. At a final step, adding random thermal noise sources $\theta(\mathbf{r}, t)$ and $\mathbf{f}(\mathbf{r}, t)$ which ensure the appropriate equilibrium correlations of ψ and \mathbf{v} to Eqs. (A.11) and (A.13), we obtain a closed set of hydrodynamic equations for ψ and \mathbf{v}

$$\frac{\partial}{\partial t} \psi = -\mathbf{v} \cdot \nabla \psi - L \nabla^2 \frac{\delta}{\delta \psi} (\beta F) + \theta, \quad (\text{A.15})$$

$$\bar{\rho} \frac{\partial}{\partial t} \mathbf{v} = -\nabla p - k_B T \psi \nabla \frac{\delta}{\delta \psi} (\beta F) + \eta_0 \nabla^2 \mathbf{v} + \mathbf{f}, \quad (\text{A.16})$$

where $\bar{\rho} = m \bar{n}_{tot}$ is the average mass density, $\eta_0 = \eta_+ + \eta_-$ is the total viscosity of the fluid, and where the incompressibility condition $\nabla \cdot \mathbf{v} = 0$ has been used in Eq. (A.15).

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